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4. Summary

1. Learning Outcomes

After studying this module, you shall be able to

- Know the fragmentation in mass spectrum
- Learn site of cleavage for different types of molecules
- Identify types of fragment
- Evaluate peaks in mass spectrum
- Analyse any mass spectrum

2. Introduction

The mass spectrum of organic molecules contains various fragment peaks in addition to the molecular ion peak. The fragments observed for a particular class of compounds have similar features.

3. Various class of compounds

3.1 Alkanes

The mass spectra of alkanes is very predictable and the stability of carbocations (or radicals) is used to predict or explain the observation of the fragment. Method of fragmentation is single bond cleavage in most cases. The molecular ion peak is strong for lower n-alkanes but its intensity fall with increase in size and branching. A regular series of fragment peaks separated by14 amu are observed in case of alkanes. There is loss of CH_2 units in series M-14, M-28, M-42 etc.

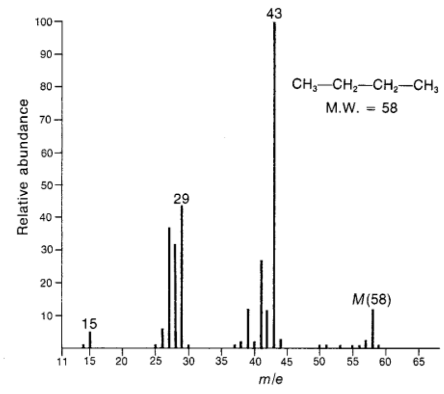


Fig 1. Mass spectrum of butane

As the carbon skeleton becomes more branched, the intensity of molecular ion peak decreases. Branched chain alkane rupture at the point of branching. Formation of tertiary favored over secondary over primary radical cations. As seen with isooctane, the molecular ion peak is very weak (figure 2).

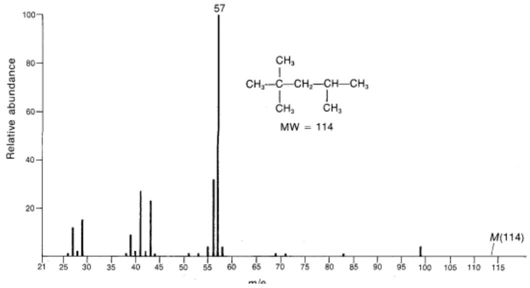


Fig 2. Mass spectrum of isooctane

Cycloalkanes

Cycloalkanes generally form strong molecular ion peaks. Fragmentation via the loss of a molecule of ethene (M-28) is common either the parent molecule or intermediate OE^{+}. Fragmentation of ring compounds requires the cleavage of two carbon-carbon bonds, which is more difficult process than the cleavage of one such bond. Therefore, a larger proportion of cycloalkane molecules than of cyclic alkane molecules survives electron bombardment without undergoing fragmentation.

3.2 Alkenes

Electron bombardment removes one of the electrons in the pi bond leaving the carbon skeleton relatively undisturbed. The alkenes have a distinct molecular ion peak which should correspond to a molecular formula with the DBE of at least one. Commonly fragmentation occurs to favor allyl cation (m/z = 41) formation (figure 3). The general formula of fragment ion in alkenes is $C_nH_{2n}^{+}$ and $C_nH_{2n-1}^{+}$.

It is sometimes difficult to locate double bonds in alkenes since they migrate readily.

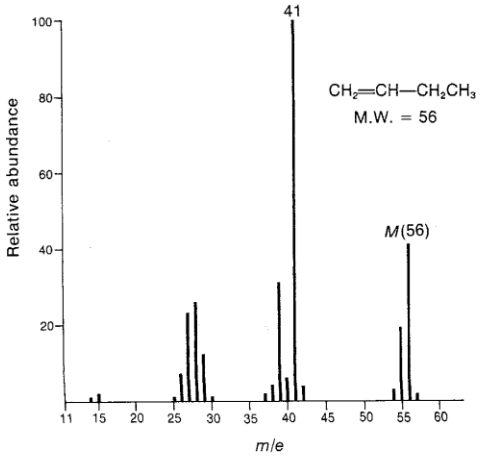


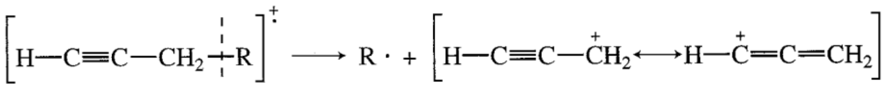
Fig. 3 Mass spectrum of 1-butene

Cycloalkenes

The mass spectra of cycloalkenes show quite distinct molecular ion peaks. For many cycloalkenes, migration of double bonds gives virtually the identical spectra. Cycloalkenes do have a characteristic fragmentation pattern that corresponds to a retro Diels-Alder reaction.

3.3 Alkynes

The molecular ion peak is very intense. As such no simple fragmentation pattern for alkynes, which can also be applied to complex molecules.



$$\left[\mathrm{H{-}C{\equiv}C{-}CH_2{-}R}\right]^{+\cdot} \longrightarrow \mathrm{R}\cdot + \left[\mathrm{H{-}C{\equiv}C{-}\overset{+}{C}H_2} \longleftrightarrow \mathrm{H{-}\overset{+}{C}{=}C{=}CH_2}\right]$$

$$\left[\mathrm{H{-}C{\equiv}C{-}R}\right]^{+\cdot} \longrightarrow \mathrm{H}\cdot + {}^{+}\mathrm{C{\equiv}C{-}R}$$

Mass spectrum of 1-pentyne shows peak for propargyl ion (m/z = 39). Terminal ion also undergo loss of terminal hydrogen to give M-1 peak. The M-1 peak in 1-pentyne appears at m/z 67 (figure 4).

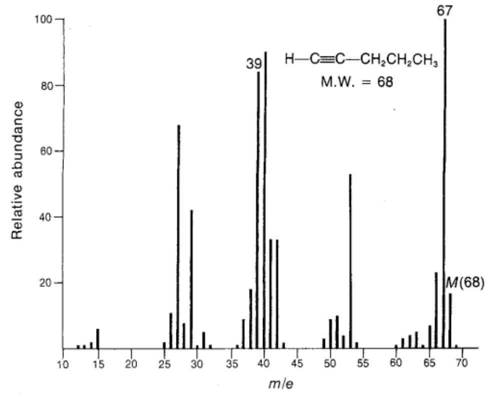


Fig 4. Mass spectrum of 1-pentyne

3.4 Aromatic Hydrocarbons

The mass spectrum has an intense molecular ion peak. Fragmentation of benzene is not observed significantly as it requires great deal of energy (figure 5).

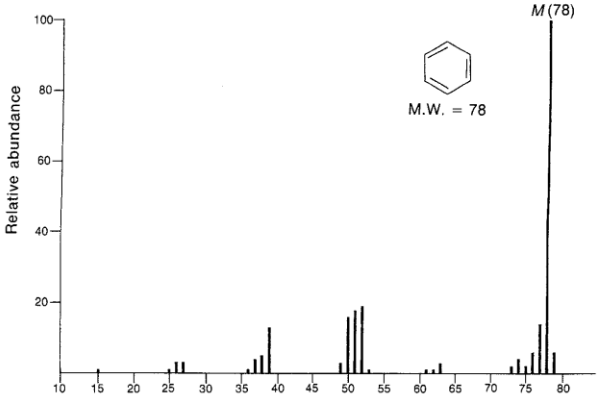
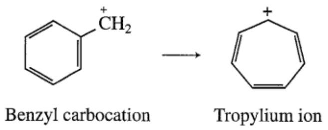


Fig 5. Mass spectrum of benzene

Alkyl benzenes: Side chain containing aromatic molecules undergo fragmentation to form benzyl cation, which rearranges to tropylium ion (m/z=91 for $C_7H_7^+$). The m/z 91 ion subsequently expels acetylene (C_2H_2) to give m/z 65peak. The tropylium ion can fragment to form cyclopentadienyl cation, which in turn, can fragment to form another equivalent of ethyne and the aromatic cyclopentadienyl cation (m/z=39).

The mass spectra of *ortho*-, *meta*-, and *para*- disubstituted aromatic rigs are essentially identical. As a result of this fact, substitution pattern in polyalkylated benzene cannot be determined by mass spectrometry.



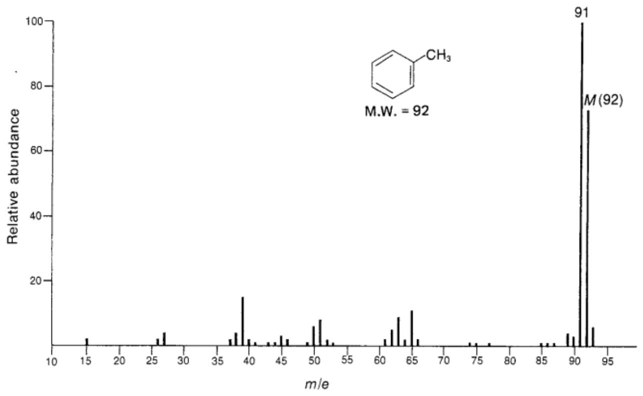
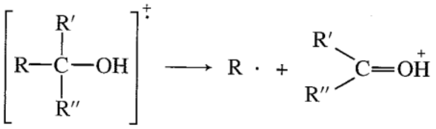


Fig 6. Mass spectrum of toluene

3.5 Alcohols and phenols

The molecular ion peak generally less intense for primary and secondary alcohols. The molecular ion peak may be absent in tertiary alcohols. The fragments are formed by the loss of alkyl group or water molecule (M-18) and α-cleavage adjacent to the hydroxyl group. The molecular ion peak in 1-butanol, 2-butanol and tert-butanol at m/z = 74 are very weak, too weak to be detected and absent, respectively (figure 7). During fragmentation the larger alkyl group is generally lost.



Dehydartion may occur by either **thermal dehydration** prior to ionization or by fragmentation of the molecular ion. Thermal dehydration is especially troublesome for alcohol samples analysed by GC-MS. The injection port of the gas chromatograph is usually maintained at more than 200 °C, and many alcohols, especially tertiary or allylic/bezylic wil dehydrate before the sample molecules even reach the GC column and certainly before the moelcules reach the ion source of the mass spectrometer. Thermal dehydration is a 1,2-elimination of water. If the alcohol molecules reach the ion source intact, however, dehydartion of the molecular ion can still occur, but in this case it is a 1,4- elimination of water via a cyclic mechanism.

Alcohols cotaining four or more carbons may undergo the simultaeneous loss of both water and ethylene. This type of fragmentation is not prominent for 1-butanolbut is responsible for the base peak at m/z=42 in the mass spectrum of 1-pentanol.

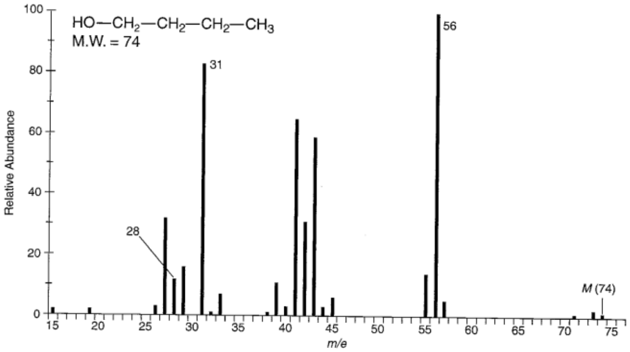


Fig 7. Mass spectrum of 1-butanol

Cyclic alcohols may undergo fragmentation by atleast three different pathways. The first fragmentation is simply α-cleavage and loss of a hydrogen atom to yield an M-1 fragment. The second fragmentation path begins with an α-cleavage of a ring bond adjacent to the hydroxyl bearing carbon, followed by a 1,5-hydrogen migration. This moves the radical site back to a resonance stabilized position adjacent to the oxonium ion. A second α-cleavage results in the loss of a propyl radical and formation of a protonated acrolein ion with m/z=57. The third fragmentation path of cyclic alcohols is dehydration via abstraction of a hydrogen atom from a three or four carbons away (the hydrogen atom is transferred in a five- or six- membered transition state) to produce a bicyclic radical cation with m/z=82.

Simple phenols give intense molecular ion peak. The common fragmentation involves loss of CO (M-28) and CHO (M-29). Phenols with alkyl side chains, undergo cleavage at benzylic bond, leading to formation of hydroxytropylium ion.

3.6 Ethers

Aliphatic ethers exhibit weak but observable molecular ion peak. Fragmentation include alpha-cleavage (m/z = 43, 59, 73 etc or M-31, M-45, M-59 etc), formation of carbocation fragments and loss of alkoxy group (inductive β-cleavage). A third type of fragmentation occurs as a rearrangement reaction of one of the fragment ions rather than the molecular ion itself. The rearrangement involves transfer of a hydrogen β to the oxonium ion with concurrent formation of an alkene. This type of rearrangement, is particularly favored when the α-carbon of the ether is branched.

The mass spectrum of diisopropyl ether has peak at m/z 87 due to alpha-cleavage. The carbon-oxygen cleavage of ether yield $C_3H_7^+$ at m/z 43 (figure 8).

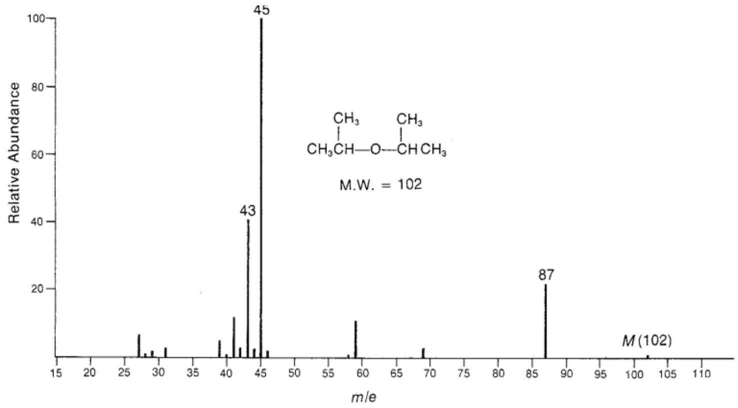


Fig 8. Mass spectrum of diisopropylether

Methylphenyl ethers undergo fragmentation at C-O bonds, with loss of CHO (M-30) and loss of CH3 (M-15).

Acetals and ketals behave very similarly to ethers. However, fragmentation is even more favorable in acetals and ketals than in ethers, so the molecular ion peak of an acetal or a ketal may either be weak or be totally absent.

Aromatic ethers except methyl ethers fragment by transfer of beta hydrogen, to give a peak at m/z 94, which expels CO to give peak at m/z 66.

3.7 **Aldehydes**

The molecular ion peak is observable but usually fairly weak (m/z = 29, 44) for aliphatic aldehydes. While aryl aldehyde give strong molecular ion peak. The fragmentation includes alpha and beta cleavage. If gamma hydrogen is present Mc-Lafferty rearrangement is also observed.

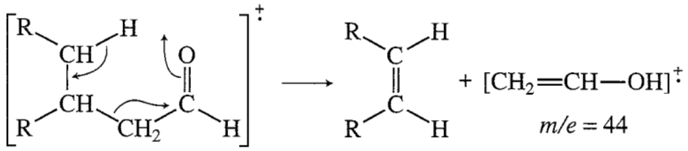
For aromatic aldehydes molecular ion peak is strong (M-1, M-29)

$$[R-CHO]^{+\cdot} \longrightarrow R-C\equiv O^{+} + H\cdot$$
$$[R-CHO]^{+\cdot} \longrightarrow H-C\equiv O^{+} + R\cdot$$

Alpha-cleavage occurs very commonly. The peak due to loss of one hydrogen atom is characteristic of aldehydes. The characteristic peak due to HCO+ observed at m/z = 29.

During beta fragmentation peak at M-43 observed.

$$\left[R \vdots CH_2-CHO\right]^{+} \longrightarrow R^{+} + CH_2=CH-O\cdot$$



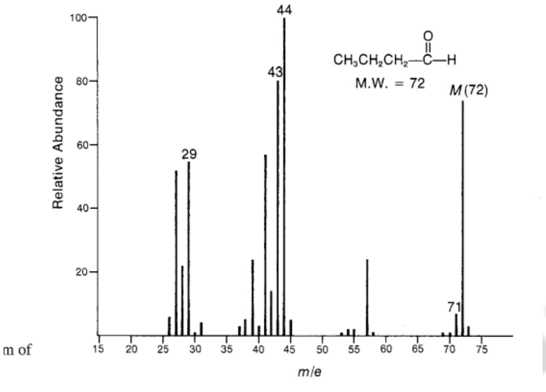
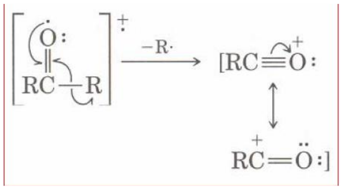


Fig 9. Mass spectrum of butanal

Aromatic aldehydes also exhibit intense molecular ion peaks, and the loss of one hydrogen atom via α-cleavage is a very favorable process. The resulting M-1 peak may in some cases be more intense than the molecular ion peak. Note the peak at m/z=77, which corresponds to phenyl cation by the loss of formyl cation.

3.8 Ketones

Ketones show an intense molecular ion peak. During fragmentation alkyl group next to carbonyl is lost, more likely the larger alkyl group is lost, with formation of RCO^+. The larger of the two alkyl groups attached to the carbonyl group appears more likely to be lost, in keeping with Stevenson’s rule.



For aliphatic ketones the fragmentation pattern shows M-15, M-29, M-43 peaks.

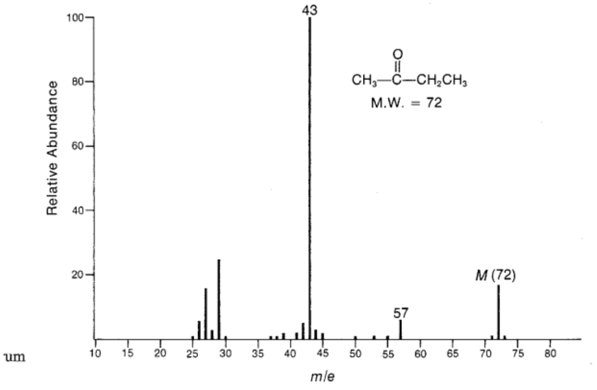
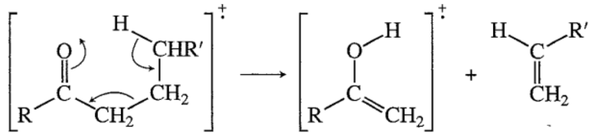
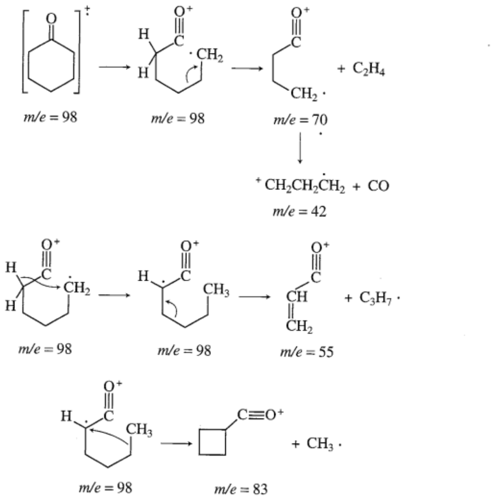


Fig 10. Mass spectrum of butanone

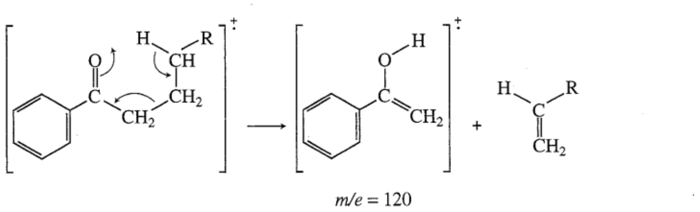
If gamma hydrogen is present then Mc Lafferty rearrangement is possible.



Cyclic ketones undergo fragmentation and rearrangement in various ways. Cyclohexanone give molecular ion peak at m/z 98. Fragmentation and rearrangement in cyclohexanone give peak at m/z 83, 70, 55, 42.



Aromatic ketones may undergo α-cleavage to lose the alkyl group and form the phenylacylium ion ($C_6H_5CO^+$, m/z=105). This ion can undergo secondary fragmentation to lose carbon monoxide, forming the $C_6H_5^+$ ion (m/z=77). Aromatic ketones may also undergo Mc Lafferty rearrangement.



3.8 Esters

Weak molecular ions observed in mass spectrum for esters as they readily undergo fragmentation. But it is usually possible to observe weak molecular ion peaks in the mass spectra of methyl esters. The esters from higher alcohols form much weaker molecular ion peaks in the mass spectra of methyl esters. The esters of higher alcohols form much weaker molecular ion peaks and esters of alcohols larger than four carbons may form molecular ion peaks that fragment too quickly to be observed. Alpha-cleavage involves loss of alkoxy group to form acylium ion. M-31, M-45, M-73 peaks are observed.

Methyl esters having gamma hydrogen undergo beta cleavage via Mc Lafferty rearrangement producing a peak at m/z=74. Ethyl, propyl, butyl and higher alkyl esters also undergo α-cleavage. In addition, however, these esters may undergo an additional rearrangement of the alkoxy portion of the ester that results in fragments that appear in the series m/z=61, 75, 89 and so on.

Benzyl esters undergo rearrangement to eliminate a neutral ketene molecule and the radical cation of benzyl alcohol at m/z=108. The resulting ion is often the most intense peak in the mass spectrum of such a compound. Alkyl benzoate esters prefer to lose the alkoxy group to form the $C_6H_5CO^+$ ion (m/z=105). This ion may lose carbon carbon monoxide to form the phenyl cation ($C_6H_5^+$) at m/z=77. Alkyl substitution on benzoate esters appears to have little effect on the mass spectral results unless the alkyl group is in the *ortho* position with respect to the ester functional group. In this case, the alkyl group can interact with the ester function, with the elimination of a molecule of alcohol.

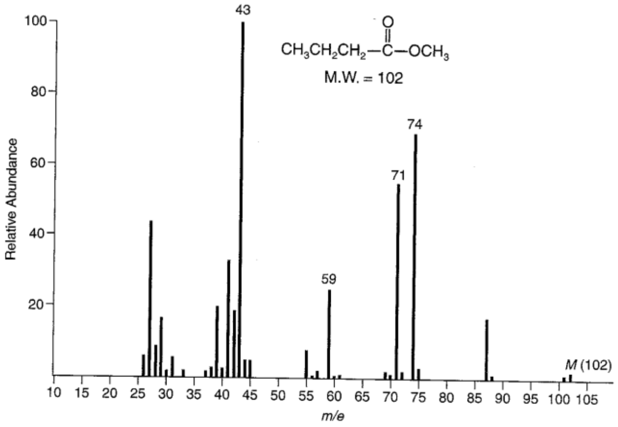
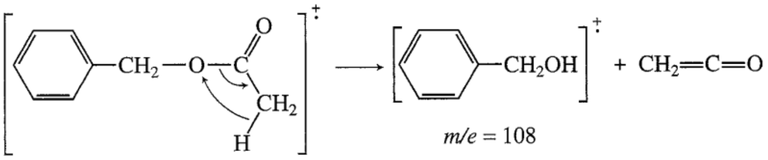


Fig.9 Mass spectrum of ethyl butyrate



3.10 Carboxylic acids

Aliphatic carboxylic acids have weak but observable molecular ion peaks (M-17, M-45). Aromatic carboxylic acids show strong molecular ion peaks. In short chain acids, alpha cleavage on either side of C=O group leads to the loss of OH and COOH. The m/z peak at 45 is due to $COOH^+$ ion.

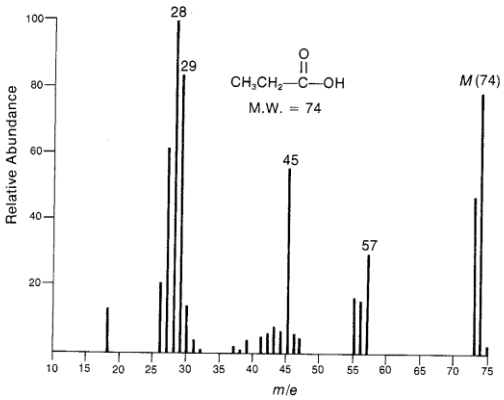
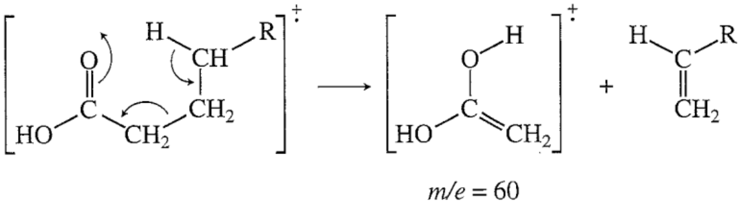


Fig. Mass spectrum of propanoic acid

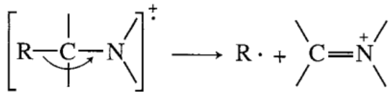
Acids containing gamma hydrogen undergo McLafferty rearrangement. In the case of carboxylic acids, this rearrangement produces a prominent peak at m/z=60.



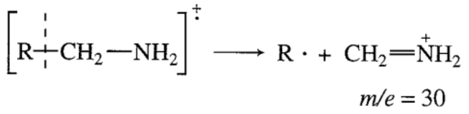
In aromatic carboxylic acids loss of OH produce $C_6H_5CO^+$ ion (m/z 105), followed by loss of CO to form $C_6H_5^+$ ion (m/z=77).

3.11 Amines

A compound with odd number of nitrogen atoms has an odd-numbered molecular weight. Thus, nitrogen rule is very important in determining whether a compound contains nitrogen or not. In aliphatic amines the molecular ion peak may be very weak or even absent. The most intense peak is due to α-cleavage. During loss of alkyl group the larger group is lost preferably.



A peak at m/z 30 observed for primary peak due to α-cleavage for $CH_2{=}NH_2^+$ formed by expulsion of a radical from molecular ion.



$$\left[R\!-\!CH_2\!-\!NH_2\right]^{+\cdot} \longrightarrow R\cdot + CH_2{=}\overset{+}{N}H_2$$

$$m/e = 30$$

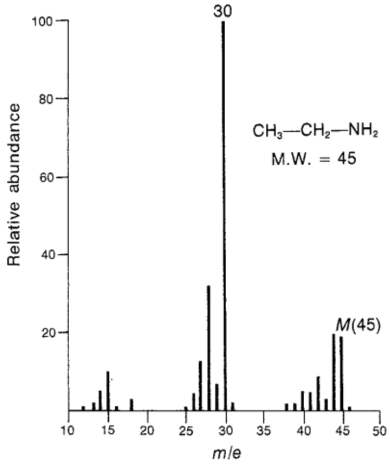


Fig. 11. Mass spectrum of ethyl amine

The presence of a peak is strong, although not conclusive, evidence that the test substance is a primary amine. The peak may arise from secondary fragmentation of ions formed from the fragmentation of secondary or tertiary amines as well. The same β-cleavage peak can also occur for long chain primary amines. Further fragmentation of the R group of the amine leads to clusters of fragments 14 mass units apart due to sequential loss of CH_2 units from the R group. Long-chain primary amines can also undergo fragmentation via the process.

This is particularly favorable when n=4 since a stable six membered ring results. In this case a fragment appears at m/z=86. Secondary or tertiary amines also undergo fragmentation processes as described earlier. The most important fragmentation process here is the β-cleavage.

Cyclic aliphatic amines usually produce intense molecular ion peaks and the main modes of fragmentation are drawn here:

Aromatic amines show intense molecular ion peaks. A moderately intense peak may appear at an m/z value one mass unit less than that of the molecular ion due to loss of a hydrogen atom. The fragmentation of aromatic amines can be illustrated for the case of aniline:

Very intense molecular ion peaks characterize substituted pyridines. Frequently, loss of a hydrogen atom to produce a peak at an m/z value one mass unit less than the molecular ion is also observed. When the alkyl side chain attached to a pyridine ring contains three or more carbons arranged linearly fragmentation via McLafferty rearrangement can also occur.

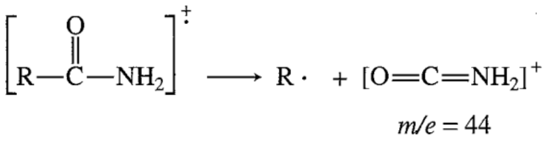
This mode of cleavage is most important for substituents attached to the number 2 position of the ring.

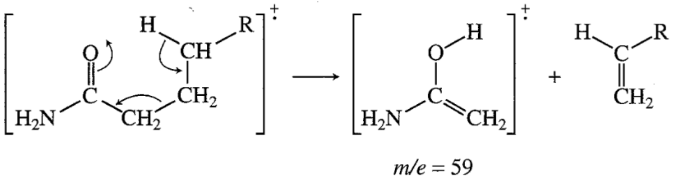
Selected Nitrogen and Sulphur compounds

As true for amines, nitrogen bearing compounds such as amides, nitriles, and nitro compounds must follow the Nitrogen rule.

3.12 Amides

Molecular ion peak is usually observable. Primary amide have fragment ion peak at m/z=44 due to β-cleavage and loss of alkyl group.





If gamma hydrogen is present then amides undergo McLafferty rearrangement. Primary amides has peak at m/z=59. For *N*-alkylamides, analogous peaks at m/z values of 73, 87, 101, and so on often appear.

3.13 Nitriles

Aliphatic nitriles usually undergo fragmentation so readily that the molecular ion peak is too weak to be observed. However, most nitriles form a peak due to the loss of one hydrogen atom, producing an ion of the type $R\text{-}CH=C=N^+$. Although this peak maybe weak, it is a useful diagnostic peak in characterizing nitriles. When the alkyl group attached to the nitrile functional group is a propyl group or some longer, the most intense peak in the mass spectrum results from a McLafferty rearrangement.

With high molecular weight nitriles, most of the fragment of the fragment ions of mass 41 are $C_3H_5^+$ ions rather than ions formed as a result of a McLafferty rearrangement. The strongest peak in the mass spectrum of an aromatic nitrile is the molecular ion peak. More important fragmentation involves loss of the elements of HCN.

3.14 Thiols and Thioethers

Thiols show molecular ion peaks that are more intense than those of the corresponding alcohols. A characteristic feature of the mass spectra of Sulphur compounds is the presence of a significant M+2 peak. This peak arises from the presence of a heavy isotope, ^{34}S, which has a natural abundance of 4.4%. The fragmentation pattern of the thiols are very similar to those of the alcohols. As alcohols tend to undergo dehydration under some conditions, thiols tend to lose the elements of hydrogen sulphide, giving rise to a M-34 peak.

Thioethers show mass spectral patterns that are very similar to those of ethers. As in the case of thiols, thioethers show molecular ion peaks that tend to be more intense than those of the corresponding ether.

3.15 Nitro compounds

The molecular ion peak for aliphatic nitro compound is generally not observed. While for aromatic nitro compounds the molecular ion peak is strong.

For aliphatic nitro compounds, peak at m/z=30 corresponds to NO^+ ion, and at m/z=46 to NO_2^+ ion **(figure 12)**.

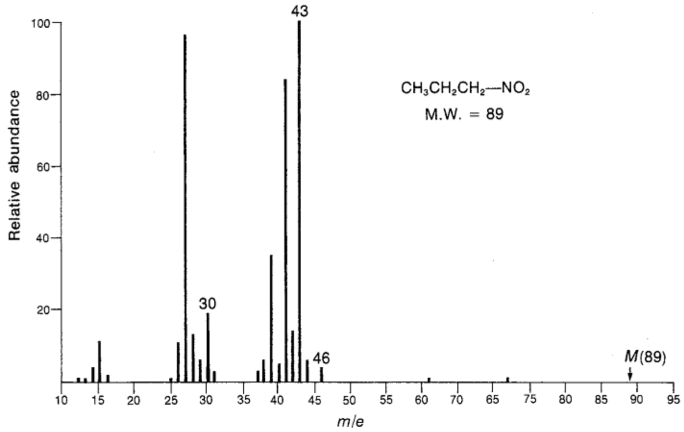


Fig 12. Mass spectrum of 1-nitropropane

3.16 Alkyl halides

Aliphatic halides have molecular ion peak strong for iodides, less strong for bromides weak for chlorides and weakest for fluorides.

Alkyl chloride and bromide have M+2 peaks, due to presence of two isotopic forms of bromine and chlorine. From the natural abundance of the isotopes of chlorine, one can conclude that if the M+2 peak is one-third the height of the molecular ion peak, then the compound contains one chlorine atom because the natural abundance of ^{37}Cl is one-third that of ^{35}Cl. Chlorine comprises of two isotopes, the isotope with a greater abundance has a mass of 35 amu (relative abundance = 75.77%) and the one with a minor abundance has a mass of 37 amu (relative abundance = 24.23%). If the M and M+2 peaks are about the same height, then the compound contains one bromine atom because the natural abundances of ^{79}Br and ^{81}Br are about the same. Bromine has a nearly 50:50 mixture of isotopes having atomic masses of 79 (relative abundance = 50.69%) and 81 amu (relative abundance = 49.31%) respectively.

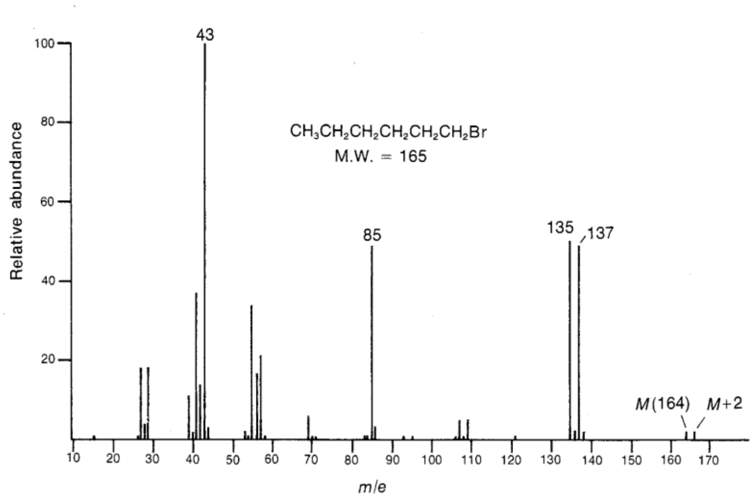


Fig 13. Mass spectrum of 1-bromohexane

Alkyl halides may also lose a molecule of HX according to the process

The mode of fragmentation is most important for alkyl fluorides and chlorides and less important for bromides and iodides.

A less important mode of fragmentation is α-cleavage, for which a fragmentation mechanism might be:

When the α-position is branched, the heaviest alkyl group attached to the α-carbon is lost with greatest facility. The peaks arising from α-cleavage are usually rather weak. A fourth fragmentation mechanism involves rearrangement and a loss of an alkyl radical:

The corresponding cyclic ion can only be observed at m/z=135 and 137 in the mass spectrum of 1-bromohexane and at m/z=105 and 107 in the mass spectrum of 2-chloroheptane. Such fragmentation is important is important only in the mas spectra of long chain alkyl chlorides and bromides.

The molecular ion peaks in the mass spectra of benzyl halides are usually of sufficient intensity to be observed. The most important fragmentation involves the loss of halogen to form $C_7H_7^+$ ion. When the aromatic ring of a benzyl halide carries substituents, a substituted phenyl cation may also appear. The molecular ion peak of an aromatic halide is generally quite intense and the most important mode of fragmentation involves loss of halogen to form the $C_6H_5^+$ ion.

4. Summary

- The mass spectra of alkanes is very predictable and the stability of carbocations (or radicals) is used to predict or explain the observation of the fragment.
- As the carbon skeleton becomes more branched, the intensity of molecular ion peak decreases in alkanes.

- Commonly fragmentation in alkenes occurs to favor allyl cation (m/z = 41) formation.
- Alkyl benzenes undergo fragmentation to form benzyl cation, which rearranges to tropylium ion (m/z 91 for $C_7H_7^+$).
- The molecular ion peak generally less intense for primary and secondary alcohols. The molecular ion peak may be absent in tertiary alcohols.
- Aliphatic ethers exhibit weak but observable molecular ion peak. Fragmentation include alpha-cleavage (m/z = 43, 59, 73 etc., or M-31, M-45, M-59 etc.,), formation of carbocation fragments and loss of alkoxy group.
- The molecular ion peak is observable but usually fairly weak (m/z = 29, 44) for aliphatic aldehydes. While aryl aldehyde give strong molecular ion peak. The fragmentation includes alpha and beta cleavage. If gamma hydrogen is present Mc-Lafferty rearrangement is also observed.
- Ketones show intense molecular ion peak. During fragmentation alkyl group next to carbonyl is lost, more likely the larger alkyl group is lost, with formation of RCO^+. If gamma hydrogen is present then Mc Lafferty rearrangement is possible.
- Weak molecular ions observed in mass spectrum for esters as they readily undergo fragmentation.
- Aliphatic carboxylic acids have weak but observable molecular ion peaks (M-17, M-45). Aromatic carboxylic acids show strong molecular ion peaks.
- A compound with odd number of nitrogen atoms has an odd-numbered molecular weight. In aliphatic amines the molecular ion peak may be very weak or even absent. The most intense peak is due to alpha cleavage.
- Molecular ion peak is usually observable. Primary amide have fragment ion peak at m/z 44 due to alpha cleavage and loss of alkyl group.
- The molecular ion peak for aliphatic nitro compound is generally not observed. While for aromatic nitro compounds the molecular ion peak is strong.
- Aliphatic halides have molecular ion peak strong for iodides, less strong for bromides weak for chlorides and weakest for fluorides. Alkyl chloride and bromide have M+2 peaks, due to presence of two isotopic forms of bromine and chlorine.